Electrochemical Hydrogenation of Soybean Oil with Hydrogen Gas

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Soybean oil has been partially hydrogenated in a proton exchange membrane (PEM) electrochemical reactor, with H_2 gas as the anode feed and source of hydrogen. The reactor is similar in design to that used in a H_2/O_2 fuel cell, with a membrane electrode assembly composed of a Pd-black powder cathode and a Pt-black powder anode fixed to the opposite surfaces of a Nafion 117 cation-exchange membrane. The PEM reactor was operated at a moderate temperature (60−90 °C) and 1 atm of pressure using commercial-grade soybean oil as the cathode feed. The effects of the current density, temperature, and oil flow rate on oil hydrogenation current efficiency and product selectivity were investigated. The oil hydrogenation current efficiency (the efficiency of electrogenerated H_2 addition to fatty acid double bonds) increased with temperature, decreased with current density, and ranged from 45 to 97%. Partially hydrogenated oil products were characterized by a low percentage of *trans*-fatty acid isomers (which are known contributors to coronary heart disease) and a moderately high concentration of saturated stearic acid (typical of nonselective, precious metal hydrogenation catalysts). An improvement in fatty acid hydrogenation selectivity was achieved by increasing the oil feed flow rate and inserting a turbulence promoter into the oil feed channel of the PEM reactor. The use of a bimetallic cathode (Pd/Co or Pd/Fe) increased the selectivity of the hydrogenation process, at the expense of a drop in current efficiency and an increase in the trans isomer content of hydro-oil products.

Introduction

Edible oils are composed primarily of triglycerides containing saturated and unsaturated fatty acids. The partial hydrogenation of fatty acid double bonds is carried out to produce a solid or semisolid fat and/or to improve the oil's oxidative stability. In soybean oil, 18-carbon fatty acids containing one, two, and three double bonds are of primary importance (see Figure 1 for the chemical structure of a typical soybean oil triglyceride). The goal of a soybean oil partial hydrogenation process is to reduce the level of 18-carbon triene fatty acid (linolenic acid, which is most reactive with O_2 from air) with the controlled production of saturated, 18-carbon stearic acid (the concentration of this high melting point fatty acid controls, to a large extent, the solid/liquid properties of an oil). The chemical catalytic hydrogenation of edible oils is carried out commercially in a stirred batch reactor operating at 150−225 °C and 10−60 psig with Raney nickel or a supported nickel catalyst.[1] Oil hydrogenation at such a high temperature leads to a number of undesirable side reactions, in particular the production of *trans*-fatty acids, which have been linked to coronary heart disease.[2,3] Lower trans isomer levels in partially hydrogenated soybean oils have been obtained with precious metal powder catalysts (e.g., Pd and Pt), but these catalysts are difficult to remove from the hydro-oil product.[4]

Two low-temperature electrochemical reaction schemes for edible oil hydrogenation have been investigated by Pintauro and co-workers. Yusem et al.[5,6] reported on the hydrogenation of soybean oil at 70−75 °C and 1 atm of

pressure in a Raney nickel powder flow-through fixed-bed electrochemical reactor. Fatty acid hydrogenation selectivities were acceptable and the concentration of *trans*-fatty acid isomers was low, as compared to the chemical catalytic process, but the method suffered from a number of drawbacks, in particular the use of a non-food-grade alcohol solvent (*tert*-butyl alcohol) and a supporting electrolyte salt. An et al.[7−9] carried out the partial hydrogenation of soybean oil in a solid polymer electrolyte proton-exchange-membrane (PEM) reactor with pure oil fed to the cathode and water as the anode feed and source of hydrogen. The efficiency for H_2 addition to the double bonds of an RBD (refined, bleached, and deodorized) soybean oil was high (up to 70% of the electrogenerated H combined with the oil) when Pd black was used as the cathode catalyst, at a constant applied current density of 0.1 A/cm^2 and a temperature of 60 °C. The trans isomers content in hydrogenated oil products was in the range of 6.5−10.5%, which is considerably lower than the 20−40% trans in oils hydrogenated catalytically, because of the low operating temperature of the electrochemical reactor.

The composition and heated oil characteristics of soybean oils that were hydrogenated electrochemically in the PEM reactor have also been examined.[10] Oils that were partially hydrogenated (20−30% reduction in double bonds) showed very low levels of degradation products (peroxides and free fatty acids). Sensory analysis of electrochemically hydrogenated oils, when heated to 190 °C, showed significantly less intensity of heated oil odor and hydrogenated odor as compared to commercially (catalytically) hydrogenated oils.

In the present study, soybean oil was hydrogenated in a PEM reactor with H_2 gas as the anode feed (rather than water). This change in reactor operation was made

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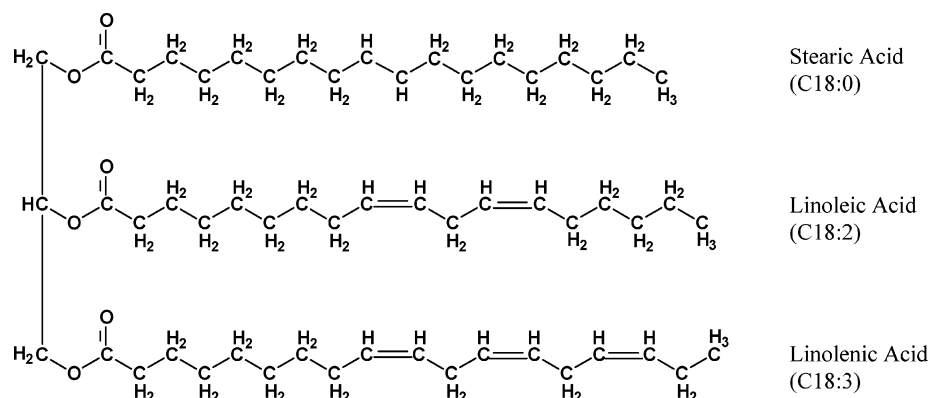‡ Tulane University.
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Figure 1. Chemical structure of an edible oil triglyceride with saturated and unsaturated 18-carbon fatty acids (all fatty acids in the cis isomer configuration).
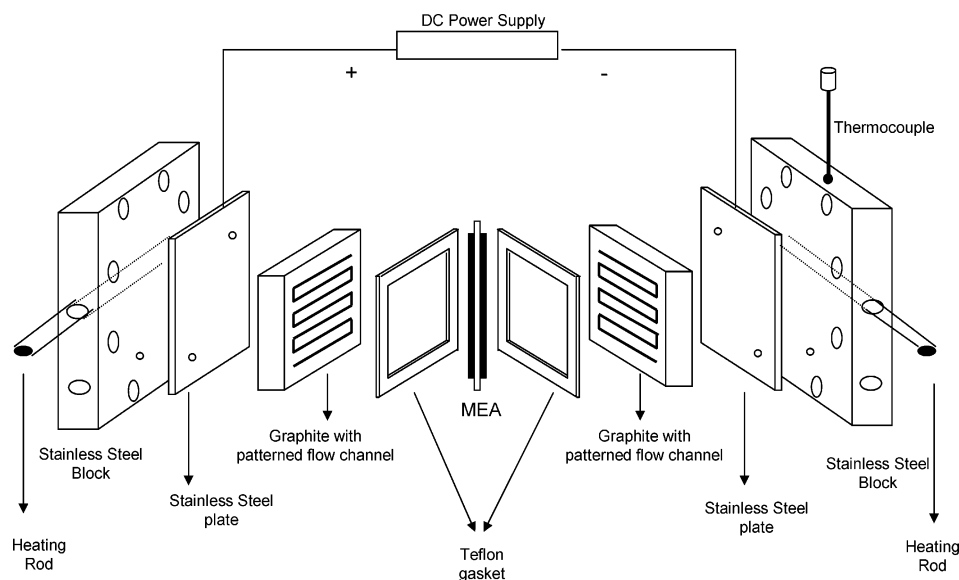

Figure 2. Exploded view of the PEM reactor for oil hydrogenation.

in order to (1) lower the power requirements of the reactor (the electrochemical production of H_2 from water is an energy-intensive reaction), (2) utilize H_2 gas that is available at existing chemical catalytic oil hydrogenation plants, and (3) identify changes, if any, in the oil hydrogenation selectivity and production rate vis-à-vis a PEM reactor operating with water.

Experimental Procedures

PEM Reactor. The key components of the PEM fuel cell reactor for edible oil hydrogenation are shown in Figure 2. The reactor consists of anolyte and catholyte flow channels separated by a thin, proton-conducting cation-exchange membrane (DuPont's Nafion 117). Porous anode and cathode electrodes, composed of catalyst powders in a polymeric binder, are attached to the opposing surfaces of the membrane, forming a "membrane electrode assembly (MEA)", similar to that employed in H_2/O_2 fuel cells.[11] Humidified H_2 gas is fed to the anode, where H_2 is oxidized electrochemically to H^+ via the reaction $H_2 \rightarrow 2H^+ + 2e^-$. Protons migrate through the ion-exchange membrane under the influence of the applied electric field and are reduced to atomic and molecular H_2 at the cathode ($2H^+ + 2e^- \rightarrow 2H \rightarrow H_2$). Electrogenerated H_2 then reacts with the unsaturated fatty acids in an edible oil, where neat (undiluted) oil is pumped along the backside of the cathode and permeates through the porous electrode structure. A portion of the electrogenerated H_2 does not react with the oil, thus lowering the current efficiency for the hydrogenation reaction. The use of the PEM reactor eliminates the need for a supporting electrolyte salt and an organic solvent for the oil feed (both of which may contaminate the hydro-oil products). The close proximity of the anode and cathode on an MEA and the high ion-exchange capacity of the hydrated ion-exchange membrane ensure facile H^+ transport during current flow and a small anode/cathode voltage drop during reactor operation (water vapor in the anode feed is absorbed into the ion-exchange membrane to maintain the membrane in a fully hydrated, ionically conductive state).

In the present study, refined, bleached, and deodorized (RBD) soybean oil (C&T Refinery, Charlotte, NC) was hydrogenated under constant-current conditions. The PEM reactor was operated in a batch recycle mode, where undiluted oil is circulated continuously through the reactor and into an external holding tank that was immersed in a constant-temperature bath. The holding tank was continuously purged with N_2 gas to eliminate oil oxidation by O_2 in air. H_2 gas was bubbled through a water bottle (maintained at the reactor temperature) to achieve near 100% humidification prior to entering the reactor (water vapor was used to hydrate the ion-exchange membrane). H_2 gas was purged after exiting

Table 1. Results from Preliminary Soybean Oil Hydrogenation Experiments (2.0 mg/cm² Pd-Black Cathode, 30 mL/min Oil Feed Flow Rate, and 1.0 atm of H₂ Pressure)

current density (A/cm²)	temp (°C)	fatty acid profile				cell voltage (V)	IV	current efficiency (%)	% trans
		C18:0	C18:1	C18:2	C18:3				
zero current (blank)[a]	70	4.2	25.4	53.5	6.7		132		0
0.10	70	25.1	26.7	33.7	3.8	0.22	91	91	8.0
0.12	70	25.7	27.1	32.7	3.7	0.25	90	82	5.8
0.14	70	26.5	27.4	31.6	3.6	0.34	88	84	6.1
0.16	70	28.2	26.9	31.1	3.7	0.30	87	81	9.2
0.20	70	22.0	30.3	32.6	3.7	0.25	92	68	10.5
			Chemical Catalytic Scheme[b]						
	140	6.0	64.1	15.9	1.2		90		41.0

[a] Fatty acid profile is the same as that for the initial oil. [b] 0.02 wt % supported Ni catalyst, 140 °C, 3.0 atm of H₂ gas pressure (data from ref 13).

the reactor. The reactor temperature and H₂ flow rate/pressure were controlled by a fuel cell test station (Fuel Cell Technologies, Inc., Albuquerque, NM).

Oil Analysis. The starting oil and hydrogenated products were analyzed using standard American Oil Chemists' Society (AOCS) methods.[12] Fatty acid profiles were determined by gas chromatographic (GC) analyses of fatty acid methyl esters (AOCS methods Ce 2-66 and Ce 1-62). Only 18-carbon fatty acids are of interest for soybean oil hydrogenation; the weight percentages of these fatty acids in the starting soybean oil were 4.2% stearic acid (18 carbons with zero double bonds, denoted as C18:0), 25.3% oleic acid (C18:1), 53.1% linoleic acid (C18:2), and 6.6% linolenic acid (C18:3). The percentage of total trans isomers in the initial soybean oil and hydrogenated oil products was determined by Fourier transform infrared spectroscopy (AOCS method Cd 14-95). The overall degree of oil hydrogenation is typically quantified by the iodine value (IV), defined as centigrams of iodine that react with 1 g of oil (I₂ reacts with the double bonds in unsaturated fatty acids). The IV for oil samples was determined directly from the GC fatty acid composition (AOCS method Cd 1c-85), using the following formula:

$$IV = 0.860 \times \% \text{ C18:1} + 1.732 \times \% \text{ C18:2} + 2.616 \times \% \text{ C18:3} \quad (1)$$

The IV of the starting soybean oil was 131; hydrogenated products will have an IV < 131.

The current efficiency for oil hydrogenation (a quantitative measure of the efficiency of electrogenerated H₂ addition to the double bonds in the oil feed) was calculated from (i) the change in the soybean oil's fatty acid composition at the conclusion of an experiment (which is directly proportional to the number of H₂ atoms that combined with the oil) and (ii) the total number of H atoms generated electrochemically on the cathode catalyst, which is equal to the total electrical charge passed in an oil experiment. The charge was calculated as the product of the constant applied current (I) and the total time of an experiment (t). Mathematically, the current efficiency (CE) equation is

$$CE (\%) = \frac{FM\left[\dfrac{2\Delta_{C18:1}}{MW_{C18:1}} + \dfrac{4\Delta_{C18:2}}{MW_{C18:2}} + \dfrac{6\Delta_{C18:3}}{MW_{C18:3}}\right]}{It} \times 100 \quad (2)$$

where $\Delta_{C18:1}$, $\Delta_{C18:2}$, and $\Delta_{C18:3}$ are the changes in the weight percent concentrations of oleic, linoleic, and linolenic fatty acids before and after a hydrogenation experiment (as obtained from GC analysis). The factors

2, 4, and 6 are the electrical equivalents for H₂ saturation of one, two, and three double bond fatty acids, respectively, M is the total mass (in grams) of soybean oil utilized in an experiment, MW is the molecular weight of each fatty acid, and F is Faraday's constant (96 487 C/equiv).

MEA Fabrication. MEAs with an apparent electrode area of 25 cm² (dimensions of 5 cm × 5 cm) were fabricated in-house by first preparing anode and cathode catalyst/binder inks. Pd-black catalyst powder (cathode) or Pt-black powder (anode) (both from Aldrich Chemical Co., Milwaukee, WI) were mixed thoroughly with specified weights of Teflon-30 [a poly(tetrafluoroethylene)/2-propanol suspension] and a commercial Nafion/2-propanol dispersion (both solutions were obtained from ElectroChem, Inc., Woburn, MA). A typical ink composition was 1.0 g of Pd-black powder (or 1.0 g of Pt black for the anode) + 0.33 g of Teflon-30 + 2.0 g of a 5 wt % Nafion dispersion. The catalyst/binder inks were coated on separate anode and cathode carbon cloth sheets (carbon cloth A-1, 0.35 mm in thickness, from E-TEK, Inc., Somerset, NJ). After evaporation of the alcohol solvent, one anode carbon sheet and one cathode carbon sheet were hot-pressed onto the opposing surfaces of a Nafion 117 cation-exchange membrane at 160 atm and 250 °F for 90 s (with the anode and cathode catalyst layers facing the membrane).[8] The final catalyst loadings were 0.5 mg/cm² for the anode and 2.0 mg/cm² for the cathode.

Results and Discussion

Preliminary Experiments. The first experiments were carried out to determine the feasibility of hydrogenating soybean oil in a PEM reactor with H₂ gas. The results in Table 1 show that soybean oils with an IV in the range of 88–92 (30–33% reduction in the number of double bonds) were synthesized in the PEM reactor at a moderate temperature (70 °C) and 1 atm of H₂ gas pressure, with a high current efficiency (68–91% for current densities of 0.1–0.2 A/cm²) and a low trans isomer content (<10.5%). In these experiments, the oil flow rate was 30 mL/min and the H₂ flow rate was 100 cm³/min. Current efficiency losses were attributed solely to H₂ gas generation at the cathode. When the rate of H generation (which is proportional to the applied current density) is greater than its consumption by reaction with the oil (which is temperature-dependent and thus constant for all experiments in Table 1), there is a build up of H on the catalyst surface, leading to H₂ formation and a bubbling off of H₂ from the electrode.
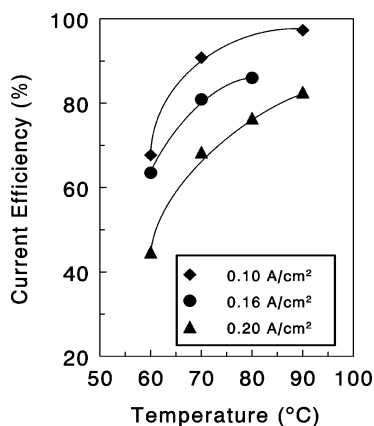
Figure 3. Effects of the temperature and current density on soybean oil hydrogenation current efficiency. Pd-black cathode, 1 atm of H_2 gas, 30 mL/min oil feed flow rate.
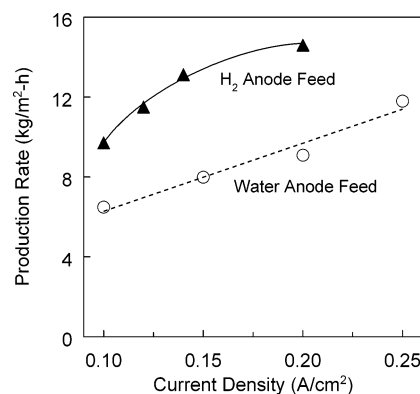

Figure 4. Variation in the production rate of a partially hydrogenated soybean oil (IV = 90) with the current density in the PEM reactor. Production rate with water as the anode feed from ref 8.

The voltage drop across the MEA was very low (0.22−0.34 V), as compared to that from oil hydrogenation with water as the anode feed (1.65−1.75 V),[8] because H_2 was not being synthesized in the PEM reactor. Because H_2 is simply being moved from the anode chamber to the cathode catalyst (by converting H_2 into H^+, transporting H^+ across the membrane, and then reacting it back to H), the anode/cathode voltage difference is only due to resistance (IR) losses in the membrane and concentration overpotentials (kinetic limitations) at the anode and cathode. The concentration of stearic acid in the oil products was high, which is typical of precious metal catalysts when used in a chemical catalytic reaction scheme.[3] High stearic acid content oils were also produced in a PEM reactor with water as the source of hydrogen.[9] There was no change in the soybean oil fatty acid profile when a zero current (blank) experiment was performed, indicating no H_2 transport across the MEA (i.e., all of the H_2 that combined with the oil was generated by the passage of current).

Effects of the Temperature and Current Density on the Current Efficiency. The effects of the current density and temperature on the soybean oil hydrogenation current efficiency were determined for an IV = 90 product. One would expect an increase in the oil hydrogenation rate with temperature,[14] and this was observed in the PEM reactor at a given (constant) current density operating condition for temperatures between 60 and 90 °C (see Figure 3). In previous electrochemical hydrogenation studies, it was found that the hydrogenation current efficiency decreased with increasing current density[8] because of an imbalance in the production and consumption rates of H_2. In the present study, a similar current efficiency/current density trend was observed, where the current efficiency decreased with a current density between 0.1 and 0.2 A/cm^2 at a constant reactor temperature. The hydrogenation current efficiencies with H_2 were always higher than those with water as the anode feed and source of H (e.g., at 60 °C, the hydrogenation current efficiency with water was 59% at 0.10 A/cm^2, 49% at 0.16 A/cm^2, and 42% at 0.20 A/cm^2).[8] The higher current efficiencies with H_2 gas were attributed to a oil/water/catalyst reaction zone of greater area at/in the cathode powder layer where protons combine with electrons and then react with the oil. It is known that (i) Nafion swells less in unit activity water vapor as compared to liquid water (the so-called "Schroeder's paradox")[15] and (ii) water accumulates at the cathode in a PEM reactor during

current flow because of electroosmotic drag of water with migrating protons (when the protons are discharged, the water remains). With less water in Nafion during an electrolysis with H_2 gas, the migration and buildup of water at the cathode is reduced, in which case there is less cathode flooding by water and a greater catalyst area for H generation and oil hydrogenation (oil molecules cannot access catalyst sites that are covered in water, but protons can react at such sites, resulting in the generation of unwanted H_2 gas that bubbles off of the electrode).

Production Rate and Power Consumption. For an electrochemical oil hydrogenation process, the size (and capital cost) of the reactors for a specific oil product output is dependent on the net production rate of hydrogenated oil per unit area of cathode. The production rate, in turn, is directly proportional to the product of the current efficiency for hydrogenation and the reactor's operating current density. The production rate per square meter of cathode area (with units of kg/m^2·h) for an IV = 90 soybean oil (i.e., a 32% reduction in the number of double bonds) was calculated using the following formula:

$$\text{production rate} = i\left(\frac{\text{CE}}{100}\right)\left(\frac{1}{0.32 \times 1.054 \times 10^6}\right) \times$$
$$(1 \times 10^4 \text{ cm}^2/\text{m}^2)(3600 \text{ s/h}) \quad (3)$$

where the current density (i) has units of A/cm^2 and the constant 1.054×10^6 is the number of coulombs of electric charge that is required to fully saturate 1 kg of soybean oil. The electrical power consumption (with units of kW·h/kg) for the production of an IV = 90 soybean oil was calculated from the operating current density, cell voltage (V), and oil production rate:

$$\text{power consumption} =$$
$$\frac{iV(2.78 \times 10^{-7} \text{ kW·h/J})(1 \times 10^4 \text{ cm}^2/\text{m}^2)(3600 \text{ s/h})}{\text{production rate}}$$
$$(4)$$

The effect of the operating current density on the production rate and power consumption for an IV = 90 oil with anode feeds of either H_2 or water at 70 °C is shown in Figures 4 and 5 (the water feed results were taken from ref 8). Higher oil production rates with H_2 as the anode feed were due to higher oil hydrogenation current efficiencies. Thus, for a given (required) hydro-oil production rate, the reactor size (i.e., electrode area)
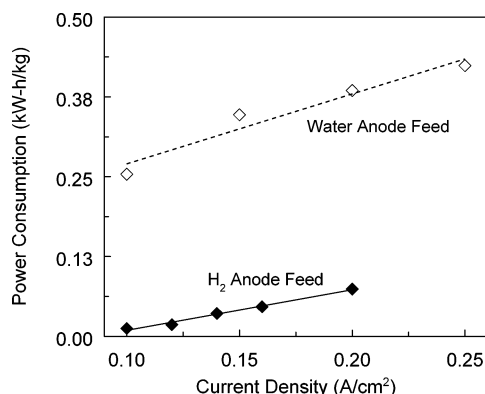
Figure 5. Dependence of the PEM reactor power consumption per kilogram of oil on the current density for an IV = 90 partially hydrogenated soybean oil. Production rate with water as the anode feed from ref 8.
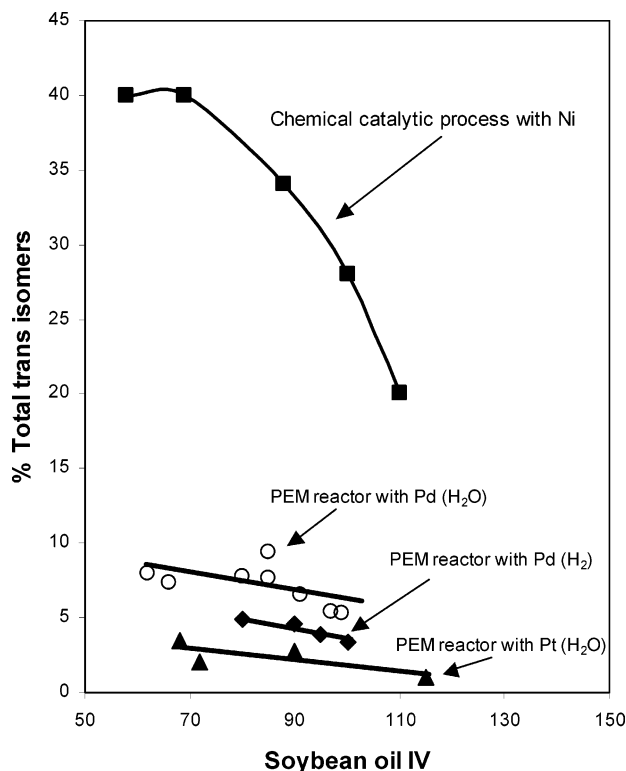

Figure 6. Variation in the total trans isomer content of partially hydrogenated soybean oils. Chemical catalytic data from ref 13. PEM reactor data with water (as the anode feed and source of hydrogen) from ref 7.
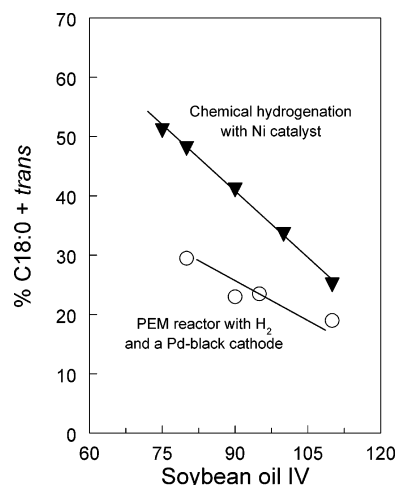

Figure 7. Total amount of 18-carbon saturated fatty acid plus total *trans*-fatty acid isomers in partially hydrogenated soybean oils. Chemical catalytic data from ref 13.

and capital cost with H_2 gas will be reduced by 33–38% as compared to a reactor that utilizes water as the source of hydrogen (e.g., 14.6 vs 9.1 kg/m^2·h at 0.2 A/cm^2 from Figure 4). The reactor power consumption with a H_2 feed was about 10 times lower than that with a water feed for all current densities examined because of the combined effects of lower cell voltages and higher oil production rates (i.e., higher oil hydrogenation current efficiencies).

Synthesis of Trans Isomers. The primary motivation for hydrogenating soybean oil electrochemically was to decrease the amount of unwanted *trans*-fatty acid isomers in an oil product. Trans isomer results are compared in Figure 6 with data from the chemical catalytic hydrogenation of soybean oil[13] (nickel catalyst, 140 °C, and 5 atm of H_2 gas) and from the electrochemical hydrogenation in a PEM reactor with water as the

anode feed and either Pd or Pt as the cathode catalyst.[7] According to GC analyses of fatty acid methyl esters in electrohydrogenated oils, trans isomers were concentrated in the trans C18:1 fatty acids. As can be seen in Figure 6, trans isomer formation is suppressed substantially in the electrochemical processes because of the combined effects of a low operating temperature and the use of a less selective precious metal catalyst cathode (less C18:1 and more C18:0 are produced with a Pd or Pt catalyst, as compared to Ni). The differences in the trans contents of oils from the Pt- and Pd-catalyzed electrochemical processes can also be attributed to selectivity of the hydrogenation reaction; i.e., oils with a Pt catalyst contained more stearic acid (C18:0), less oleic acid (C18:1), and consequently less trans isomers.[7]

Some edible oil processors prefer to evaluate a hydrogenated oil product in terms of the sum of trans isomers and saturated 18-carbon fatty acids. The C18:0 plus total trans contents for various IV soybean oils are compared in Figure 7 for the PEM reactor process with H_2 and from a high-temperature chemical process with a Ni catalyst.[13] Clearly, the electrochemical scheme is producing a healthier oil product because of a significant reduction in trans isomer generation.
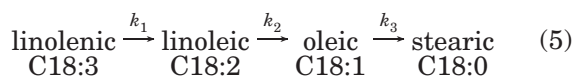
Selectivity Studies. From a close inspection of the fatty acid profiles in Table 1, it is obvious that a partially hydrogenated oil (IV = 90) from the PEM reactor contains more stearic and linolenic acids than products from a high-temperature, chemical catalytic hydrogenation process with a nickel catalyst. These two fatty acid constituents should be lower (or at least be controllable) if the PEM reactor product is to have commercial utility. In the present study, two methods were examined to improve the fatty acid selectivity during soybean oil hydrogenation in the PEM reactor: (i) increasing the oil flow rate to minimize the contact time with the catalyst and (ii) modifying the catalyst surface to alter oil adsorption.

To compare the hydrogenation selectivity in the PEM reactor with that from other process schemes in the literature that produce oils of different IVs, the linolenate, linoleate, and oleate fatty acid selectivities[16] (denoted as S_{Ln}, S_{Lo}, and S_O, respectively) were determined. These selectivities are based on the following simplified first-order irreversible reaction sequence for

Table 2. Effect of the Oil Flow Rate on Soybean Oil Hydrogenation Selectivity and Cis/Trans Isomerization (2.0 mg/cm² Pd-Black Cathode, 0.16 A/cm², 1.0 atm of H₂ Pressure, and 70 °C)

flow rate (mL/min)	fatty acid profile (%)				IV	current efficiency(%)	S_{Ln}	S_{Lo}	S_O	% trans
	C18:0	C18:1	C18:2	C18:3						
initial oil	4.2	25.4	53.5	6.7	132					0
30	18.4	28.0	38.8	4.0	102	80	1.35	0.71	0.96	6.2
57	17.9	28.7	38.5	4.0	102	79	1.32	0.76	1.00	7.3
85	20.3	27.9	37.1	4.0	99	100	1.20	0.71	0.85	6.4
108	18.5	28.0	38.3	4.0	101	93	1.30	0.71	0.93	6.0
140	18.8	28.4	37.7	4.1	100	87	1.20	0.74	0.88	6.2
140 (with turbulence promoter)	15.0	33.6	36.9	3.4	100	70	1.52	1.19	1.81	15.0

the hydrogenation of unsaturated 18-carbon fatty acids:

$$\underset{\substack{\text{C18:3}}}{\text{linolenic}} \xrightarrow{k_1} \underset{\substack{\text{C18:2}}}{\text{linoleic}} \xrightarrow{k_2} \underset{\substack{\text{C18:1}}}{\text{oleic}} \xrightarrow{k_3} \underset{\substack{\text{C18:0}}}{\text{stearic}} \quad (5)$$

where k_1, k_2, and k_3 are pseudo-first-order rate constants. The relative rates of the individual reactions are quantified in terms of three selectivities:

$$S_{Ln} = \frac{k_1}{k_2}, \quad S_{Lo} = \frac{k_2}{k_3}, \quad S_O = \frac{k_1}{k_3} \quad (6)$$

where the following differential rate equations can be written for the hydrogenation reaction sequence

$$\frac{d[\text{oleic}]}{dt} = k_2[\text{linoleic}] - k_3[\text{oleic}] \quad (7)$$

$$\frac{d[\text{linoleic}]}{dt} = k_1[\text{linolenic}] - k_2[\text{linoleic}] \quad (8)$$

$$\frac{d[\text{linolenic}]}{dt} = -k_1[\text{linolenic}] \quad (9)$$

Integration of the above rate equations, given the initial concentrations of the four C18 fatty acids, results in the following algebraic equations:

$$[\text{linolenic}]_t = [\text{linolenic}]_{t=o}e^{-k_1 t} \quad (10)$$

$$[\text{linoleic}]_t = [\text{linolenic}]_{t=0}\left(\frac{k_1}{k_2 - k_1}\right)(e^{-k_1 t} - e^{-k_2 t}) + [\text{linoleic}]_{t=0}e^{-k_2 t} \quad (11)$$

$$[\text{oleic}]_t = [\text{linolenic}]_{t=0}\left(\frac{k_1}{k_2 - k_1}\right)\left(\frac{k_2}{k_3 - k_1}\right)(e^{-k_1 t} - e^{-k_3 t}) - [\text{linolenic}]_{t=0}\left(\frac{k_1}{k_2 - k_1}\right)\left(\frac{k_2}{k_3 - k_2}\right)(e^{-k_2 t} - e^{-k_3 t}) + [\text{linoleic}]_{t=0}\left(\frac{k_2}{k_3 - k_2}\right)(e^{-k_2 t} - e^{-k_3 t}) + [\text{oleic}]_{t=0}e^{-k_3 t} \quad (12)$$

The rate constants k_1, k_2, and k_3 were determined using the known time of an oil hydrogenation experiment in the PEM reactor, the initial and final concentrations of linolenic, linoleic, and oleic acids, and eqs 10−12. From these rate constants, the fatty acid hydrogenation selectivities were determined.

Oil Flow-Rate Effects. A series of oil hydrogenation experiments were performed to assess the influence of oil mass transfer (through the carbon cloth current collector) on reaction selectivity. When the oil flow rate

is increased, triglyceride transport in to and out of the current collector should increase, thus shortening the contact time of oil with the Pd cathode and limiting the extent of hydrogenation. To assess this effect, experiments were carried out in the PEM reactor (operating at 70 °C, 1.0 atm of H₂ pressure, and 0.10 A/cm²) at an oil feed flow rate ranging from 30 to 140 mL/min (linear velocities of 25−117 cm/s based on the width and depth of the oil flow channel) and by insertion of a turbulence promoter (a stainless steel screen) in the oil feed channel. For these experiments, the cathode catalyst was 2.0 mg/cm² Pd black and the current collector was carbon cloth type A-1 (0.35 mm in thickness). In a blank test with no Pd catalyst, the mesh was shown to have no catalytic activity for the electrohydrogenation of soybean oil.

The fatty acid profiles, IVs, current efficiencies, selectivities, and % trans isomers of oil products from these experiments are listed in Table 2. The hydrogenation product distribution did not change significantly with increasing oil flow rate, but there was an improvement in the selectivity at the highest flow rate (140 mL/min) with the addition of the turbulence promoter (a decrease in C18:0 by ≈20%, an increase in C18:1 of ≈18%, and a decrease in C18:3 by ≈17%). Not unexpectedly, the % trans isomers in the oil product increased with increasing reaction selectivity (i.e., as the C18:1 concentration increased, more trans isomers were produced). There was some loss in current efficiency when the turbulence promoter was employed in the reactor, indicating an increase in H₂ gas evolution from the cathode when the contact time of oil with the catalyst is shortened.

The best (highest) soybean oil fatty acid selectivities in Table 2 are contrasted with those from five chemical catalytic hydrogenation schemes in Table 3. A distinguishing characteristic of the PEM reactor process is the relatively small values of S_{Lo} and S_O. The concentration of mono-unsaturated C18:1 product is not as high as that from a batch slurry reactor with Ni or Pd/C due to a large value of k_3, which drives the electrohydrogenation reaction to a fully saturated stearic acid product. Likewise, the low value of S_O is due to the large value of k_3, as compared to k_1. The similarity in all S_{Ln} values means that both the chemical catalytic and electrochemical processes are performing equally well in converting C18:3 fatty acid to C18:2.

Modified Cathode Catalysts. It is known that the performance and selectivity of a noble metal hydrogenation catalyst can be altered by the addition of metal modifiers or promoters.[21] Bimetallic Pd catalysts, for example, have been used to improve the reaction selectivity for the chemical catalytic hydrogenation of acetylene to ethylene and butadiene to 1-butene.[22] In the present study, bimetallic cathode MEAs were investigated, where a second metal (either cobalt or iron)

Table 3. Comparison of Selectivities and the Trans Isomer Contents for Partially Hydrogenated Soybean Oil

process	product IV	S_{Ln}	S_{Lo}	S_O	% trans
PEM reactor with H_2 (fatty acid profile from Table 2, 140 mL/min with turbulence promoter)	100	1.52	1.19	1.81	15.0
Chemical Catalytic Processes					
Ni catalyst, slurry reactor, 140 °C/44 psig[13]	110	1.84	11.3	20.8	20
Pt/Al$_2$O$_3$ catalyst, slurry reactor, 60 °C, 145 psig[17]		1.35	0.85	1.15	
Pd/C catalyst, slurry reactor, 60 °C, 27.5 psig[18]	118	1.70	8.3	14.1	22.2
Pd/Al$_2$O$_3$ catalyst, fixed-bed reactor, 80 °C, 17.8 psig[19]	110	1.62	0.75	1.22	8
Pd/C catalyst, fixed-bed reactor, 170 °C, 50 psig[20]	112	.80	1.40	1.12	17

Table 4. Soybean Oil Hydrogenation Fatty Acid Profiles with a Modified Pd Catalyst Cathode (0.10 A/cm², 1.0 atm of H$_2$ Pressure, 70 °C, 140 mL/min Oil Feed Flow Rate)

cathode conditions	fatty acid profile (%)				IV	selectivity			% trans	current efficiency (%)
	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$		S_{Ln}	S_{Lo}	S_O		
base case: no cathode modification and no TP[a]	28.2	26.9	31.1	3.7	87	0.96	0.71	0.68	9.2	81
	25.1	26.7	33.7	3.8	91	1.06	0.67	0.70	8.0	91
	18.4	28.0	38.8	4.0	102	1.35	0.71	0.96	6.2	80
TP[b] and no cathode modification	18.1	37.7	29.3	2.3	89	1.51	1.49	2.24	19.2	69
	17.0	38.2	30.6	2.7	93	1.39	1.59	2.21	12.0	60
	15.8	35.3	34.7	3.4	99	1.33	1.35	1.79	14.7	69
	9.3	32.7	43.2	4.5	115	1.53	1.59	2.44	11.8	59
with TP and Pd/Co cathode	15.2	42.9	29.3	1.7	92	1.91	2.31	4.39	20.0	80
	12.8	40.3	33.7	2.4	99	1.84	2.18	4.00	18.0	65
	10.0	35.2	40.0	3.7	109	1.68	1.74	2.92	16.0	65
	7.5	30.6	45.9	5.1	119	1.35	1.46	2.13	7.0	84
with TP and Pd/Fe cathode	15.9	45.2	27.5	1.1	90	2.27	2.64	5.99	20.0	72
	11.7	40.1	34.9	2.3	101	2.04	2.26	4.62	16.0	76
	9.1	34.1	40.8	3.5	109	1.93	1.51	2.90	12.0	70
	7.2	31.3	46.0	4.8	119	1.77	1.76	3.12	6.0	68

[a] TP denotes turbulence promoter.

was electrodeposited in situ on Pd black after MEA fabrication. Our rationale for adding the second metal was to alter the triglyceride adsorption on the catalyst, thereby shortening the time of catalyst/oil contact, which, in turn, should decrease the amount of saturates in the hydro-oil product.

To fabricate a bimetallic cathode MEA, a Nafion 117 membrane was first immersed in a salt solution of either 0.5 M CoSO$_4$ or 0.5 M FeSO$_4$ for 24 h, during which time the H$^+$ counterions in Nafion (i.e., those cations associated with the membrane's SO$_3^-$ ion-exchange sites) were exchanged by metal cations from the external salt solution. After equilibration, the membrane was thoroughly washed with deionized and distilled water to remove Co^{2+} or Fe^{2+} (and their accompanying anions) not associated with the membrane's fixed charges. Treated Nafion membranes were then used as the solid polymer electrolyte for MEA fabrication, using the same general procedure as that described in the Experimental Section of this paper. After anode and cathode hot-pressing to the membrane, the MEA was mounted in the PEM reactor and N$_2$ gas was pumped through the cathode feed channel while humidified H$_2$ gas was circulated past the anode. The reactor was then operated at a constant current density of 1.31 mA/cm². H$^+$ electrogenerated at the cathode migrated through the membrane and displaced absorbed metal ions. When the migrating Co^{2+} or Fe^{2+} reached the cathode, it was reduced to Co or Fe. Metal plating was continued for sufficient time to allow all metal ions inside the membrane to be electrochemically deposited on the Pd cathode (a total charge of 10.6 C accomplished this task). On the basis of the metal ion content in the Nafion membrane, the cathode loading of Co or Fe was 0.9–1.0 mg/cm² (with 2.0 mg/cm² of Pd). After the metal reduction step, RBD soybean oil was circulated past the cathode and a normal batch-recycle oil hydrogenation experiment was carried out at 70 °C, atmospheric

pressure, and an oil flow rate of 140 mL/min (with an oil feed channel turbulence promoter).

A comparison of fatty acid profiles, current efficiencies, and hydrogenation selectivities for Pd, Pd/Co, and Pd/Fe cathodes is given in Table 4 for product IVs ranging from about 90 to 120. The results show that (i) fatty acid hydrogenation selectivities improved after the addition of the second metal (there was a decrease in both stearic and linolenic fatty acids for a given IV), (ii) current efficiencies with the modified cathodes were lower than those observed with pure Pd black (this result is consistent with our earlier finding that the efficiency of H$_2$ addition to the oil decreases when less fully saturated stearic acid is produced), (iii) the selectivities for a Pd/Co and Pd/Fe catalyst were essentially the same, and (iv) there is an increase in the trans isomer content when the reaction selectivity was improved (because most of the trans isomers are confined to the C18:1 fatty acid, any increase in this oil component will result in an increase in the trans content). There was no consistent trend in hydrogenation current efficiency with charge passed (i.e., there was no evidence of catalyst deactivation as the hydrogenation was extended to produce a lower IV oil product). Each experiment in Table 4 used a new MEA, and differences in current efficiencies were attributed to random variations in the condition/structure of the MEA.

Conclusions

Soybean oil has been partially hydrogenated in a PEM electrochemical reactor (similar to that used in a H$_2$/O$_2$ fuel cell) with H$_2$ gas as the anode feed and source of hydrogen. The key component of the reactor is a MEA, composed of a Pd-black powder cathode and Pt-black powder anode that were hot-pressed onto the opposite surfaces of a Nafion 117 cation-exchange membrane. The PEM reactor was operated in a batch-recycle mode

at a moderate temperature and 1 atm of pressure using commercial-grade RBD soybean oil as the cathode feed. The effects of the current density (0.1–0.2 A/cm^2), temperature (60–90 °C), and oil feed flow rate on the oil hydrogenation rate and product selectivity were investigated. The oil hydrogenation current efficiency (the efficiency of electrogenerated H$_2$ addition to fatty acid double bonds) increased with the temperature, decreased with the current density, and ranged from 45 to 97%. Partially hydrogenated oil products were characterized by a low percentage of *trans*-fatty acid isomers (which are known contributors to coronary heart disease) and a moderately high concentration of saturated stearic acid (typical of a nonselective hydrogenation). The total concentration of stearic acid plus trans isomers in a range of electrohydrogenated soybean oil products was 20–40% lower than that from a high-temperature chemical hydrogenation process with Ni catalyst. An improvement in fatty acid hydrogenation selectivity was achieved by operating the reactor at a high oil feed flow rate with a turbulence promoter in the PEM reactor's oil feed channel. The use of a bimetallic cathode (Pd/Co or Pd/Fe) increased the selectivity of the hydrogenation process vis-à-vis the use of a Pd-black cathode (oil products had a lower concentration of saturated stearic acid, a lower concentration of triene linolenic acid, and a higher concentration of mono-unsaturated linoleic acid). Whenever the selectivity increased, however, there was a drop in the current efficiency and an increase in the trans isomer content of the hydro-oil products.

Acknowledgment

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